Very Efficient Photoinduced Electron Transfer at Gold Electrodes Modified with Self-Assembled Monolayers of Porphyrin-Ferrocene-Thiol Linked Molecules

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Introduction. It is very important to mimic the natural systems for the realization of a highly efficient artificial photosynthetic device. We have demonstrated that the highly efficient photo-induced up-hill electron transfer can be achieved at gold electrodes modified with self-assembled monolayers (SAMs) of molecules containing porphyrin and electron relay groups such as quinone and ferrocene [1-3]. We have proposed that one of the most important reasons for the very high efficiency of this system is the effective inhibition of energy and/or reverse electron transfer from excited porphyrin to the gold as a result of the highly ordered structure of the SAM [3,4].

In this work, three compounds (Fig. 1), which have porphyrin, ferrocene and thiol groups as sensitizer, electron relay and surface binding groups, respectively, separated from each other by alkyl chains are studied. While the chain length between thiol and ferrocene was kept constant, that between ferrocene and porphyrin was varied. Quantum efficiency of photoinduced electron transfer at the gold electrode modified with SAMs of these molecules was examined. In addition, effects of introduction of various metals into porphyrin ring on photoelectrochemical characteristics was investigated

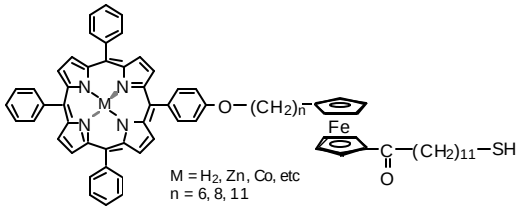

Fig. 1 Molecules used in this study.

Experimental. $PC_nFcC_{11}SH$ (M = H_2, Zn and Co; n = 6, 8, 11 in Fig. 1) were synthesized [3,4]. The gold surface was modified by dipping the substrate in dichloromethane solution containing 1 mM $PC_nFcC_{11}SH$ at 20 °C for 15 h under Ar atmosphere. A 500 W Xe lamp with a monochromator was used as a light source. Introduction of the metal into porphyrin ring was carried out by immersing the $PC_nFcC_{11}SH$ SAM modified gold into methanol containing 1 mM metal acetate.

Results and Discussion. At the gold electrodes modified with the SAMs of $PC_nFcC_{11}SH$, cathodic photocurrent flowed in 0.1 M $NaClO_4$ containing 5.0 mM MV^{2+} as an electron acceptor as soon as the electrode was illuminated as far as potential was more negative than +600 mV, i.e., the redox potential of ferrocene moiety [5]. They were very stable for long time and fell instantly when illumination was switched off. Calculated quantum efficiencies at –200 mV based on the absorbed photons were 4.0 %, 11 % and 12 % at the gold electrodes modified with the SAMs of $PC_6FcC_{11}SH$, $PC_8FcC_{11}SH$ and $PC_{11}FcC_{11}SH$, respectively. The quantum efficiencies depended on alkylchain length of the molecules. The longer the alkylchain between porphyrin and ferrocene in the SAM, the larger the photocurrent. The present results indicate that energy and/or reverse electron transfer from excited porphyrin to ferrocene and/or gold play important roles for determining the efficiency.

Effects of introduction of various metals into porphyrin ring on photoelectrochemical characteristics will be also discussed.

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